

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08G 69/48, 69/44, C08K 5/353, 5/357		A1	(11) International Publication Number: WO 96/34909 (43) International Publication Date: 7 November 1996 (07.11.96)
(21) International Application Number: PCT/NL96/00172			(81) Designated States: AL, AU, BB, BG, BR, CA, CN, CZ, EE, GE, HU, IS, JP, KP, KR, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).
(22) International Filing Date: 18 April 1996 (18.04.96)			
(30) Priority Data: 9500406 4 May 1995 (04.05.95) BE			
(71) Applicant (<i>for all designated States except US</i>): DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).			Published <i>With international search report.</i>
(72) Inventors; and			
(75) Inventors/Applicants (<i>for US only</i>): LOONTJENS, Jacobus, Antonius [NL/NL]; Synagogeplantsoen 76, NL-6231 KK Meerssen (NL). DERKS, Franciscus, Johannes, Marie [NL/NL]; In de Hoven 12, NL-6093 DK Heythuysen (NL). SHAM, Chi, Keung [GB/NL]; Bergstraat 60, NL-6174 RS Schinnen (NL).			
(74) Agent: ALFENAAR, Marinus; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).			
(54) Title: HIGH-MOLECULAR POLYAMIDE			
(57) Abstract			
The invention relates to a process for the preparation of a high-molecular polyamide by adding a bislactam and a bisoxazoline or bisoxazine to the melt of a polyamide of a lower molecular weight. An increased and very stable melt viscosity is obtained. The invention also covers a polyamide composition which comprises both bislactam and bisoxazoline or bisoxazine.			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

HIGH-MOLECULAR POLYAMIDE

5

The invention relates to a process for the preparation of a high-molecular polyamide by mixing polyamide of a lower molecular weight with a bislactam 10 in the melt.

Such a process is known from various patent publications, in general involving the addition of 0.2-10 wt.% of the bislactam to the polyamide. It is remarkable that the increase in the molecular weight 15 strongly differs in the various publications and may vary between an increase in the inherent viscosity of nylon 6 from 1.62 to 4.00 (JP-A-01197526) and from 1.24 to 1.55 (JP-A-01236238) upon addition of 0.8-1.0 wt.% of N,N'-terephthaloyl-bis- ϵ -caprolactam to the melt.

20 The increase in the molecular weight in these cases appears to be highly dependent on the balance between the proportions of acid and amino end groups in the polyamides started from.

Since this balance is highly dependent on, 25 among other factors, the conditions of preparation of the polyamide, e.g. the use of chain terminators or in balance of the initial monomers, the processor who wishes to obtain an enhanced molecular weight by using a bislactam as chain extender will either have great 30 problems with the reproducibility of the final molecular weight or be obliged to have extensive analyses performed on each batch of initial polyamide and adjust his recipes to the results. This is undesirable where high productivity at low costs is 35 sought.

Another drawback of these known compositions is that the melt viscosity varies strongly with the residence time in the melt.

The object of the invention therefore is a process which does not have said drawbacks and provides, in a simple reproducible manner, with a minimum of recipe adaptations, a significant increase in the molecular weight of a polyamide which is maintained in the melt for a fairly long time.

This object of the invention is achieved if besides the bislactam a bisoxazoline and/or a bisoxazine is/are also used as chain extender.

The process for the preparation of a high-molecular polyamide by adding a bislactam to the melt of a polyamide of a lower molecular weight is characterized in that moreover a bisoxazoline and/or a bisoxazine is/are added.

It is known from DE-B-2458733 that addition of a bisoxazoline and/or a bisoxazine results in an increase in the molecular weight of the polyamide. However, in general the effect is small and time dependent.

Highly surprisingly, the process according to the invention results in a more than additive effect where the increase in melt viscosity is concerned, as well as in a very stable and reproducible melt viscosity.

The invention also covers a polyamide composition comprising:

- 30 a. one or more polyamides
- b. a bislactam
- c. a bisoxazoline and/or a bisoxazine.

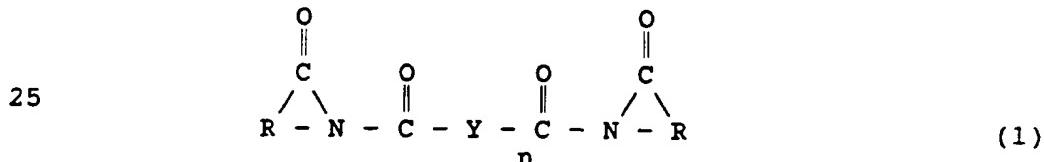
The process according to the invention is in general suitable for all polyamides which are melt processable. The process is highly suitable for (semi)crystalline polyamides, for instance the aliphatic polyamides, such as nylon 4, nylon 4,6, nylon

6, nylon 7, nylon 6,6, nylon 8, nylon 9, nylon 8,10 etc. The best results are achieved with polyamides obtained by ring-opening polymerization of lactams, for instance poly(ϵ -caprolactam), also called nylon 6, and 5 poly(laurolactam), nylon 12, or by polycondensation of α,ω -amino acids.

Special benefits can be obtained in the case of polyamide homopolymers and copolymers that contain units derived from an aromatic dicarboxylic acid and an 10 aliphatic diamine, which have a relatively low polymerization rate. Examples of these (co)polyamides are 6.T, nylon 6.I/6.T, nylon 6/6.T, nylon 6.I/6.T/2MP.T or nylon 6/6.6/6.T in which T = terephthalic acid, I = isophthalic acid and 2 15 MP.T = 2-methylpentamethyleneterephthalic diamide.

The composition according to the invention also includes copolyamides.

Bislactams which amongst others are suitable for the process according to the invention have the 20 following general formula:



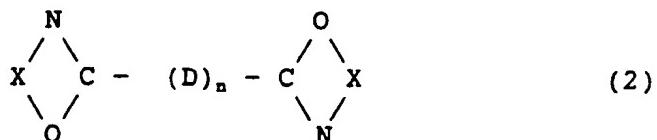
where Y = a bivalent alkylene group or an aromatic 30 group, R = an alkylene group and n = 0 or 1.

Examples of compounds having the above formula are N,N'-isophthaloyl bis-2-caprolactam, N,N'-adipoyl bis- ϵ -caprolactam, N,N'-terephthaloyl bis-laurolactam and N,N'-isophthaloyl bisbutyrolactam.

35 These compounds can be synthesized simply by reacting the corresponding carboxylic acid dihalide with lactam in the presence of an amine or an inorganic base, for instance KOH.

The bisoxazoline and bisoxazine have the general formula:

5



10 where X = a bivalent group and the ring is a 5-ring or 6-ring for bisoxazoline and bisoxazine, respectively. X is for instance an ethylene group, a substituted ethylene group, a trimethylene or a substituted trimethylene group. As substituent, for instance an alkyl group with 1 to 10 carbon atoms, an aryl group, a cycloalkyl group or an aralkyl group may be present.

15 Examples of an alkyl group are methyl, ethyl, hexyl, aklylhexyl, nonyl, etc., of an aryl group are phenyl, naphthyl, diphenyl, etc. and an example of a cycloalkyl 20 group is cyclohexyl.

D is a bivalent organic group, for instance an alkylene group, an arylene group, a cycloalkylene group and an aralkylene group.

n = 0 or 1.

25 Examples of bisoxazolines and bisoxazines are 2,2'-bis(2-oxazoline), 2,2-bis(4-methyl-2-oxazoline), 2,2'-bis(4-phenyl-2-oxazoline), 2,2'-bis(4-hexyl-oxazoline), 2,2'-p or m-phenylene bis(2-oxazoline), 2,2'-tetramethylene bis(4,4'-dimethyl-2-oxazoline) and 30 the corresponding oxazines.

Preference is given to 2,2'-bis(2-oxazoline), 2,2'-p- phenylene bis(2-oxazoline), 2,2'-m-phenylene bis(2-oxazoline) and the corresponding oxazines.

These oxazolines and oxazines can be prepared 35 simply by means of ring closure of the corresponding bisamide alcohol with a dehydration agent, for instance concentrated sulphuric acid or thionyl chloride or by means of ring closure of the corresponding bisamide

halide with a base. Another simple process of preparation is that in which a dinitrile and ethanol or propanol amine are heated to approx. 180°C in the presence of a Lewis acid. The preparation processes are 5 not limited to said methods, however.

The quantity of bislactam that is used in the process according to the invention in general amounts to at least 0.1 part by weight per 100 parts by weight of polyamide. Depending on the polyamide chosen, the 10 desired increase in molecular weight or melt viscosity, and the bislactam, the required amount may vary between wide limits, for instance between 0.1 and 5 parts by weight per 100 parts by weight of polyamide, preferably between 0.3 and 3 parts by weight per 100 parts by 15 weight of polyamide. In special cases, for instance if the polyamide started from has a very low molecular weight, for instance Mn = 5000 or less, a larger amount of bislactam may be required.

The quantity of bisoxazoline or bisoxazine 20 used in the process according to the invention in general amounts to at least 0.1 part by weight per 100 parts by weight of polyamide. Depending on the polyamide chosen, the desired increase in molecular weight or melt viscosity, and the bisoxazoline or 25 bisoxazine, respectively, the required amount may vary between wide limits, for instance between 0.1 and 4 parts by weight per 100 parts by weight of polyamide, preferably between 0.2 and 2.5 parts by weight per 100 parts by weight of polyamide.

30 If a quantity larger than 5 or 4 parts by weight, respectively, is added, the viscosity will increase to such an extent in certain cases that normal processing is not possible any more, or, by contrast, the viscosity increasing effect is reduced.

35 The person skilled in the art will be able to determine the optimum quantities in a given situation by means of simple systematic experiments.

The composition may further also contain the usual additives for instance stabilizers, colorants, processing agents, such as release agents and antistatic agents, and nucleants, for instance talcum, 5 and filling or reinforcing materials, for instance mineral fillers, such as mica, organic fibres, such as aramid fibres, and mineral fibres, such as glass fibres, and flame retardants.

The process can be carried out in a simple 10 manner, for instance by mixing the polyamide, the bislactam and the bisoxazoline or bisoxazine in solid form, after which the mixture is molten in for instance a Haake kneader, a Brabender mixer or an extrusion apparatus. The various components may also be supplied 15 directly to the melting apparatus or the bislactam and bisoxazoline and/or bisoxazine may be first pre-mixed in solid form and then added to the polyamide melt.

A preferred embodiment of the invention is one in which in the polymerization process for 20 producing the polyamide at the end of polymerization column the bislactam and the bisoxazoline or bisoxazine, is introduced and mixed into the polymerizing melt shortly before leaving the column. In another preferred embodiment the extruder to be used 25 for melt mixing the bislactam and the bisoxazoline or bioxazine is placed directly at the exit of the polymerization column and the molten polyamide leaving the polymerization column is mixed before being solidified.

30 The invention will now be elucidated by means of the following non-restrictive examples.

Materials used:

- a.1. polyamide 4.6, STANYL®: $\eta_{rel} = 2.8$ (1 gram in
35 100 ml of formic acid) from DSM, the Netherlands
- a.2. polyamide 6, AKULON® F-124 $\eta_{rel} = 2.5$ from

DSM, the Netherlands

- b. N,N'-terephthaloyl bislaurolactam
- c.1. 2,2'-m-phenylene bis(2-oxazoline), Takeda
Chemicals Japan (BPO)
- 5 c.2. 2,2'-m-phenylene bis(2-oxazine)

Procedure:

The polyamides were molten with the bisoxazoline or bisoxazine and/or the bislactam in a Haake Rheocoral 90
10 kneader, chamber volume 50 ml and 80 rpm. For polyamide
6 the temperature was set to 240°C and for polyamide
4,6 to 300°C. The torque of the kneader was measured at
several points in time.

The tested compositions and the results of the
15 measurements are listed in table 1.

TABLE 1

Experiment	1	2	3	4	Example I	5	6	7	8	Example II	9	Example III	10	Example IV
5	a.1.	100	100	100	100									
	a.2.					100	100	100	100	100	100	100	100	
b.				2						1.5	1.5	1.5	1.5	
c.1.									0.5		0.5			
c.2.				1.5	1.5						0.5	1.0		
													1.5	
10	kneader torque (Nm)													
	4 min.	2.5	1.3	4.3	6.5	2.5	3.0	6.6	10.2	12.0				
	6 min.						2.0	3.2	5.9	10.2	12.5	14.8		
	10 min.						2.4	4.1	5.2	10.2	12.4	14.8		
	20 min.						3.0	5.5	4.5	8.8	11.5			

5

10

15

Experiments 1-4 show the effect of the addition to polyamide 4,6 of the bislactam and bisoxazine, if added separately and if both are present, exp. 4, example 1. A significantly higher 5 torque than to be expected on the basis of (comparative) experiments 2 and 3 was found in example I.

Example II (exp. 8) as well shows the more than additive effect of the combination of oxazoline 10 and bislactam on the melt viscosity of polyamide 6. It is very remarkable that the melt viscosity remains stable at the high level for a long time.

Due to the high melt viscosity and its stability, the compositions according to the invention 15 are particularly suitable for extrusion and blow molding applications for the manufacture of for instance film and stock shapes.

In a further experiment compositions based on 20 nylon-6 have been processed over a single screw extruder and the effect of presence of caprolactam and cyclic and linear oligomers in the polyamide has been studied.

Extrusion conditions have been: Temperature profile 25 from hopper to die: 200, 235, 250--250°C. Screw speed: 200 rpm. Without vacuum venting.

The chain extender was tumbled on the polyamide without any adhering oil. The tumbled granules were dosed into the hopper with a gravimetric device.

30 Results are given in Table 2.

TABLE 2

Sample characteristic	[NH ₂] mmol/kg	[COOH] mmol/kg	RSV m/m%	CL m/m%	CYCLIC OLIGOMER						LINEAR OLIGOMER			
					2-mer m/m%	3-mer m/m%	4-mer m/m%	5-mer m/m%	6-mer m/m%	2-mer ppm	3-mer ppm	4-mer ppm	5-mer ppm	6-mer ppm
Nylon-6 (as recovered) in washed extruder	57	51	2.25	8.10	0.38	0.48	0.44	0.39	0.35	80	116	161	215	271
	55	50	2.27	7.76	0.31	0.49	0.43	0.38	0.34	71	106	156	196	248
after washing	55	52	2.41	0.02	0.03	0.09	0.15	0.22	0.31	<4	22	76	153	213
0.3% BPO/0.5% IBC extruded	40	39	2.69	8.00	0.33	0.47	0.43	0.38	0.32	33	41	62	75	92
(after washing)	33	42	2.88	0.03	0.01	0.06	0.13	0.20	0.27	<4	9	37	52	76

BPO is 2,2'-m-phenylene bis(2-oxazoline)

IBS Isophthalic biscaprolactam

Compared to the blank experiment, in which the unwashed nylon-6 was extruded without any chain extender, a significant increase of the relative viscosity, measured in formic acid (RSV), is realized in the 5 presence of the chain extender combination of the invention. After washing the oligomer content is lower.

In a further experiment the influence of mixing intensity on the effectiveness of the chain extension was studied. For this purpose the effect of a 10 double screw, (DS), vs. a single screw, (SS), extruder under the conditions given previously was studied. The results are given in Table 3.

TABLE 3

Sample characteristic	[NH ₂] mmol/kg	[COOH] mmol/kg	RSV m/m%	CL m/m%	CYCLIC OLIGOMER						LINEAR OLIGOMER			
					2-mer m/m%	3-mer m/m%	4-mer m/m%	5-mer m/m%	6-mer m/m%	2-mer ppm	3-mer ppm	4-mer ppm	5-mer ppm	6-mer ppm
F124 (as received)	55	52	2.45	0.08	0.02	0.08	0.15	0.23	0.33	17	25	63	137	221
F124 (SS Blank)	56	49	2.51	0.19	0.02	0.08	0.15	0.23	0.32	54	62	93	149	218
F124/0.3% BPO/ 0.5% IBC (SS)	41	39	3.02	0.37	0.02	0.08	0.15	0.23	0.31	29	30	45	65	98
F124/0.6% BPO/ 1% IBC (SS)	29	34	3.77	0.56	0.02	0.08	0.15	0.23	0.31	8	6	9	14	21
F124/1% BPO/1.5% IBC (SS)	43	21	3.67	0.68	0.02	0.07	0.15	0.23	0.30	<4	<5	<6	<8	<9
F124 (DS Blank)	56	47	2.53	0.11	0.02	0.008	0.15	0.23	0.32	66	71	113	156	213
F124/0.3% bpo/0.5% Ibc (DS)	41	38	2.92	0.27	0.02	0.08	0.15	0.23	0.31	36	42	57	77	109
F124/0.6% BPO/1% IBC (DS)	29	37	3.61	0.13	0.02	0.08	0.15	0.23	0.30	10	13	20	24	35
F124/1% BPO/1.5% IBC (DS)	29	35	3.69	0.15	0.02	0.09	0.15	0.23	0.30	<4	<5	<6	<8	<10

5

10

15

F124 is the nylon-6 of the previous example after washing twice with water.

- 5 Except the caprolactam content, (CL)*, the results are practically identical, indicating that the process of chain extension is very fast and not limited by transport.

This makes the process applicable in existing polymerisation columns that are provided at the end of the column with a simple mixing device, for instance 10 for mixing colorants or other additives into the polymer melt, without disturbing the prop stream regime of the polymerisation column.

A well-known method for producing high molecular weight nylons is by aftercondensing in the 15 solid phase the polyamide obtained from the polymerization process in the melt phase. This process is very time consuming and some by-products, sometimes resulting in discoloration of the polyamide are formed. Very surprising the nylon-6 obtained by the process of 20 the present invention contains significantly less caprolactam than the high molecular weight nylon-6 after aftercondensing in the solid phase which makes the high molecular nylon-6 produced according to the invention more fit for application in food packaging.

C L A I M S

1. Process for the preparation of a high-molecular
5 polyamide by adding a bislactam to the melt of a
polyamide of a lower molecular weight,
characterized in that moreover a bisoxazoline
and/or a bisoxazine is/are added.
2. Process according to claim 1, characterized in
10 that the bislactam has been derived from an
aromatic dicarboxylic acid and ε-caprolactam or
laurolactam.
3. Process according to claim 1 or 2, characterized
in that the bisoxazoline and/or the bisoxazine
15 is/are chosen from the group consisting of 2,2'-
bis(2-oxazoline), 2,2'-p- phenyl bis(2-oxazoline),
2,2'-m-phenylene bis(2-oxazoline) and the
corresponding oxazines.
4. Process according to claim 1, characterized in
20 that the quantity of bislactam added is between
0.1 and 5 parts by weight and the quantity of
bisoxazoline and/or bisoxazine between 0.1 and 4
parts by weight per 100 parts by weight of
polyamide.
- 25 5. Process for the preparation of a high molecular
weight polyamide by polymerising the monomers for
the repeating units in the polyamide in the melt
under conventional conditions, characterized in by
adding at the end of the polymerization process a
30 bislactam and a bixoxazoline or a bisoxazine to
the melt.
6. Polyamide composition comprising:
 - a. 100 parts by weight of polyamide
 - b. 0.1-5 parts by weight of a bislactam
 - 35 c. 0.2-4 parts by weight of a bisoxazoline and/or
bisoxazine.

- 15 -

7. Process as described in the specification and examples.
8. Polyamide composition as described in the specification and examples.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/NL 96/00172

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G69/48 C08G69/44 C08K5/353 C08K5/357

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08G C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 8604 Derwent Publications Ltd., London, GB; Class A, AN 86-025650 XP002008682 & JP,A,60 248 730 (UNITIKA KK) , 9 December 1985 see abstract</p> <p>---</p> <p>DATABASE WPI Section Ch, Week 8604 Derwent Publications Ltd., London, GB; Class A23, AN 86-025651 XP002008683 & JP,A,60 248 731 (UNITIKA KK) , 9 December 1985 see abstract</p> <p>---</p> <p>-/-</p>	
A		

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- 'A' document defining the general state of the art which is not considered to be of particular relevance
- 'E' earlier document but published on or after the international filing date
- 'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

'&' document member of the same patent family

Date of the actual completion of the international search 17 July 1996	Date of mailing of the international search report 29.07.96
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentstaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Leroy, A

INTERNATIONAL SEARCH REPORT

Inte	ntal Application No
PCT/NL 96/00172	

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 008, no. 168 (C-236), 3 August 1984 & JP,A,59 068330 (TAKEDA YAKUHIN KOGYO KK), 18 April 1984, see abstract --- & EP,A,0 097 937 (TAKEDA) 11 January 1984	
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 569 (C-666), 15 December 1989 & JP,A,01 236238 (TEIJIN LTD), 21 September 1989, cited in the application see abstract ---	
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 494 (C-651), 8 November 1989 & JP,A,01 197526 (TEIJIN LTD), 9 August 1989, cited in the application see abstract ---	
A	DE,B,24 58 733 (HULS) 24 July 1975 cited in the application -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 96/00172

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-B-2458733	24-07-75	DE-A- 2458733	24-07-75